

NON-AQUEOUS ELECTROLYTIC SOLUTION
AND LITHIUM SECONDARY BATTERY

FIELD OF THE INVENTION

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The present invention relates to a non-aqueous electrolytic solution favorably employable for a non-aqueous lithium secondary battery.

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BACKGROUND OF THE INVENTION

At present, a non-aqueous secondary battery such as a lithium secondary battery (particularly, lithium ion secondary battery) is generally employed as an electric source for driving a small electronic device. The non-aqueous secondary battery comprises a positive electrode, a non-aqueous electrolytic solution, and a negative electrode. The non-aqueous lithium ion secondary battery preferably comprises a positive electrode of lithium complex oxide such as LiCoO_2 , LiMn_2O_4 , or LiNiO_2 , a non-aqueous electrolytic solution such as a solution of electrolyte in a carbonate solvent such as ethylene carbonate (EC) or propylene carbonate (PC), and a negative electrode of carbonaceous material or lithium metal. Recently, the carbonaceous material such as coke or graphite has been paid much attention, because a negative electrode of carbonaceous material hardly forms thereon deposition of lithium metal in the form of dendrite and therefore hardly produces an electric short circuit with a positive electrode. Further, no liberation of lithium metal from the negative electrode occurs.

The non-aqueous secondary battery preferably has good battery characteristics such as large electric discharge capacity and high electric discharge retention. For instance, in a non-aqueous lithium ion secondary battery using a positive electrode of LiCoO_2 , LiMn_2O_4 , or

LiNiO₂, oxidative decomposition of a portion of the non-aqueous electrolytic solution undergoes in the electric charging stage. The decomposition product disturbs electrochemical reaction so that the electric discharge capacity decreases. It is considered that the oxidative decomposition takes place in the non-aqueous solvent of the non-aqueous electrolytic solution on the interface between the positive electrode and the electrolytic solution.

Moreover, in a non-aqueous lithium ion secondary battery using negative electrode of carbonaceous material of high crystallinity such as natural graphite or artificial (or synthetic) graphite, reductive decomposition of the solvent of the non-aqueous electrolytic solution undergoes on the surface of the negative electrode in the charging stage. The reductive decomposition on the negative electrode undergoes after repeated charging-discharging procedures even in the case of using a cyclic carbonate such as ethylene carbonate (EC) and propylene carbonate (PC) which is a preferably employed solvent of the electrolytic solution.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a non-aqueous electrolytic solution which is favorably employable for the preparation of a non-aqueous lithium secondary battery, particularly a non-aqueous lithium ion secondary battery.

It is another object of the invention to provide a non-aqueous secondary battery such as a lithium ion secondary battery which has improved discharge capacity retention.

The present invention resides in a non-aqueous electrolytic solution comprising at least two organic compounds dissolved in a solvent comprising a cyclic carbon-

ate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each organic compound,

5 in which both of said two organic compounds have a reduction potential higher those of the cyclic and chain carbonates, and

10 in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V).

15 In the non-aqueous electrolytic solution of the invention, the one organic compound preferably has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.05 V.

20 The invention further resides in a non-aqueous secondary battery which comprises a positive electrode comprising lithium complex oxide, a negative electrode comprising graphite, a non-aqueous electrolytic solution containing an electrolyte salt in a non-aqueous solvent, and a separator, in which the non-aqueous electrolytic solution comprises at least two organic compounds dissolved in a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each compound, in which both of said two organic compounds have a reduction potential higher than those of the cyclic and chain carbonates, and in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V).

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DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in more detail.

5 The present invention is characterized by incorporation of at least two organic compounds into a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each compound. Both of the two organic compounds have a reduction potential higher than those of
10 the cyclic and chain carbonates, and one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V, more preferably
15 less than 0.05 V).

The above-mentioned two or more organic compounds are preferably selected from the group consisting of a carbonate compound, a sultone compound, a sulfonate compound, a sulfone compound, and phenyl acetylene.

20 Examples of the carbonate compounds include vinylene carbonate, methyl propargyl carbonate, and benzaldoxime carbonate.

Examples of the sultone compounds include 1,3-propanesultone and 1,4-butanedisultone.

25 Examples of the sulfonate compounds include 1,4-butanediol dimethane sulfonate and ethylene glycol dimethane sulfonate.

Examples of the sulfone compounds include divinyl sulfone.

30 The two or more organic compounds are preferably employed in such manner that one organic compound is a carbonate compound, and another organic compound is a sultone compound, a sulfonate compound, or a sulfone compound. Particularly, it is preferred that one organic
35 compound is vinylene carbonate or methyl propargyl carbonate, and another organic compound is 1,3-propanedisultone.

tone, 1,4-butanestultone, 1,4-butanediol dimethane sul-
fonate, or ethylene glycol dimethane sulfonate. It is
also preferred that one organic compound is benzaldoxime
methylcarbonate and another organic compound is divinyl-
5 sulfone. It is also preferred that one organic compound
is a sulfonate compound and another organic compound is a
sultone compound. It is also preferred that one organic
compound is 1,4-butanediol dimethanesulfonate or ethylene
glycol dimethanesulfonate, and another organic compound
10 is 1,3-propanesultone or 1,4-butanestultone. It is also
preferred that one organic compound is phenylacetylene,
and another organic compound is vinylene carbonate, 1,3-
propanesultone, or 1,4-butanestultone.

It is preferred that the addition of the above-de-
15 scribed two or more organic compounds is made to a non-
aqueous solvent comprising one or more cyclic carbonates
and one or more chain carbonates. Examples of the cyclic
carbonates include ethylene carbonate (EC), propylene
carbonate (PC), and butylene carbonate (BC). Examples of
20 the chain carbonates include dimethyl carbonate (DMC),
diethyl carbonate (DEC), methyl ethyl carbonate (MEC),
and methyl isopropyl carbonate (MIPC). Other known non-
aqueous solvents such as tetrahydrofuran, 2-methyltetra-
hydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-di-
25 ethoxyethane, 1,2-dibutoxyethane, γ -butyrolactone, aceto-
nitrile, methyl propionate, and dimethylformamide may be
incorporated into the mixture of the cyclic carbonate and
the chain carbonate. The mixture solvent of the non-
aqueous electrolytic solution preferably contains the
30 combination of the cyclic carbonate and chain carbonate
at least 60 weight %, more preferably at least 80 weight
%, and most preferably at least 90 weight %. In the non-
aqueous solvent mixture and in the combination of the
cyclic carbonate and the chain carbonate, the cyclic car-
35 bonate preferably is in an amount of 5 to 70 volume %,
and the chain carbonate preferably is in an amount of 95

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to 30 volume %.

In the non-aqueous electrolytic solution of the invention, the combined two or more organic compounds having a reduction potential higher than the non-aqueous solvent are considered to function in the following manner.

In the electric charging stage, the combined organic compounds having a high reduction potential decomposes on the surface of a negative electrode almost at the same time or with a short interval, prior to the decomposition of the solvent material. The products produced by the decomposition of the organic compounds (i.e., additives) deposits on the surface of the negative electrode to cover the surface with an inactive material, which reduces decomposition of the solvent material. If the amount of the additive is larger than a certain level, however, the function of the electrolytic solution lowers.

The non-aqueous electrolytic solution preferably comprises further an electrolyte salt (particularly, inorganic electrolyte salt) such as LiPF_6 , LiBF_4 , LiClO_4 , $\text{CF}_3\text{SO}_2\text{Li}$, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiPF}_4(\text{CF}_3)_2$, $\text{LiPF}_3(\text{CF}_3)_3$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$, $\text{LiPF}_5(\text{iso-C}_3\text{F}_7)$, and $\text{LiPF}_4(\text{iso-C}_3\text{F}_7)_2$. The electrolyte salts can be employed singly or in combination. Generally, the electrolyte salt can be incorporated into the non-aqueous solvent in such an amount to give an electrolytic solution of 0.1M to 3M, preferably 0.5M to 1.5M.

The non-aqueous secondary battery of the invention comprises a positive electrode and a negative electrode in addition to the non-aqueous electrolytic solution.

The positive electrode generally comprises a positive electrode active material and an electro-conductive binder composition.

The positive electrode active material preferably is a complex metal oxide containing at least one metal element selected from the group consisting of cobalt, manga-

nese, nickel, chromium, iron, and vanadium and a lithium element. Examples of the complex metal oxides include LiCoO_2 , LiMn_2O_4 , and LiNiO_2 .

5 The electro-conductive binder composition can be produced by a mixture of an electro-conductive material such as acetylene black or carbon black, a binder such as polytetrafluoroethylene (PTFE) or poly(vinylidene fluoride) (PVDF), and a solvent. For the preparation of a positive electrode, the mixture is coated on a metal
10 plate such as aluminum foil or stainless plate, dried, and pressed for molding. The molded product is then heated *in vacuo* at a temperature of approx. 50 to 250°C for approx. 2 hours, to give the desired positive electrode.

15 The negative electrode comprises a negative electrode active material such as a lithium metal, a lithium alloy, carbonaceous material having a graphite-type crystalline structure which can absorb and release lithium ion, or a complex tin oxide. Examples of the carbonaceous materials include thermally decomposed carbonaceous
20 materials, cokes, graphites (e.g., artificial graphite and natural graphite), fired organic polymer materials, and carbon fibers. Preferred are carbonaceous materials having a graphite-type crystalline structure in which the
25 lattice distance of lattice surface (002), namely, d_{002} , is in the range of 0.335 to 0.340 nm. The negative electrode active material in the powdery form such as carbonaceous powder is preferably used in combination with a binder such as ethylene propylene diene terpolymer
30 (EPDM), polytetrafluoroethylene (PTFE) or poly(vinylidene fluoride) (PVDF).

There are no specific limitations with respect to the structure of the non-aqueous secondary battery of the invention. For instance, the non-aqueous secondary
35 battery can be a battery of coin type comprising a positive electrode, a negative electrode, and single or plural

separators, or a cylindrical or prismatic battery comprising a positive electrode, a negative electrode, and a separator roll. The separator can be a known microporous polyolefin film, woven fabric, or non-woven fabric.

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The present invention is further described by the following non-limiting examples.

[Measurement of Reduction Potential]

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Ten mg of graphite powder (MCMB6-28, produced by Osaka Gas Chemical Co., Ltd.) is mixed with 10 wt.% of polyvinylidene fluoride (binder). The mixture is placed in N-methylpyrrolidone to give a slurry. The slurry is coated on a electro-collector stainless steel plate (surface area: 2 cm²). Thus coated plate is set as a working electrode to form a triode cell in combination with counter and reference electrodes using lithium metal.

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A non-aqueous solvent is prepared from ethylene carbonate and methyl ethyl carbonate at a volume ratio of 3:7. To the solvent is added LiPF₆ (electrolyte, to give 1 M concentration) to produce an electrolytic solution. To the resulting electrolytic solution is added an organic compound (i.e., additive) to be measured, in an amount of 2 wt.%.

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The triode cell is placed in the additive-containing electrolytic solution, and the reduction potential is measured at room temperature under a potential scanning rate of 1 mV/sec. A potential in terms of V at which a current of 0.5 mA flows is assigned to the reduction potential.

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The reduction potentials measured on various organic compounds are set forth in Table 1.

Table 1

	Organic Compound (Additive)	Abbr.	Reduction Potential (vs. lithium metal)
5	Vinylene carbonate	VC	0.81 V
	1,3-Propanesultone	PS	0.83 V
	1,4-Butanesultone	BS	0.80 V
10	1,4-Butanediol dimethane sulfonate	BDDMS	0.81 V
	Ethylene glycol dimethane sulfonate	EGDMS	0.81 V
	Methyl propargyl carbonate	MPGC	0.82 V
15	Phenylacetylene	PA	0.81 V
	Benzaldoxime carbonate	BAOMC	1.78 V
	Divinylsulfone	VS	1.45 V

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[Example 1]

1) Preparation of non-aqueous electrolytic solution

In a non-aqueous mixture of propylene carbonate and dimethyl carbonate [PC:DMC=1:2, volume ratio] was dissolved LiPF₆ to give a non-aqueous electrolytic solution of 1 M concentration. To the electrolytic solution were added vinylene carbonate (VC) and 1,3-propanesultone (PS), both in an amount of 1.5 wt.% (based on the amount of the electrolytic solution).

2) Preparation of lithium secondary battery and measurement of its battery characteristics

LiCoO₂ (positive electrode active material, 80 wt.%), acetylene black (electro-conductive material, 10 wt.%), and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture was further added N-methylpyrrolidone (solvent). Thus produced positive electrode mixture was coated on aluminum foil, dried, molded under pressure, and heated to give a positive

electrode.

Natural graphite (negative electrode active material, 90 wt.%) and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture was further
5 added N-methylpyrrolidone (solvent). Thus produced negative electrode mixture was coated on copper foil, dried, molded under pressure, and heated to give a negative electrode.

The positive and negative electrodes, a microporous
10 polypropylene film separator, and the non-aqueous electrolytic solution were combined to give a coin-type battery (diameter: 20 mm, thickness: 3.2 mm).

The coin-type battery was charged at room temperature (20°C) with a constant electric current (0.8 mA) to
15 reach 4.2 V, and then the charging was continued under a constant voltage of 4.2 V for a period of 6 hours. Subsequently, the battery was discharged to give a constant electric current (0.8 mA). The discharge was continued to give a terminal voltage of 2.7 V. The charge-dis-
20 charge cycle was repeated 50 times.

The initial discharge capacity was as much as 0.97 which was calculated on the basis that the initial discharge capacity measured in Comparison Example 6 (using a solvent mixture consisting of ethylene carbonate, propyl-
25 ene carbonate and diethyl carbonate, 3/1/6, volume ratio) was set to 1.

After the 50 cycle charge-discharge procedure, the discharge capacity was 94.8% of the initial discharge capacity. No deformation was observed on the battery
30 appearance. The low temperature characteristics were satisfactory.

The preparation and evaluation of the battery are summarized in Table 2.

35 [Comparison Example 1]

The procedures of Example 1 were repeated except

that neither VC nor PS were incorporated into the electrolytic solution.

In performing the charging procedure using the secondary battery, propylene carbonate (PC) decomposed at the first charging procedure, and no discharge was done. The battery was deformed. The battery was then disjointed to examine its interior. The graphite negative electrode showed exfoliation on its surface.

The preparation and evaluation of the battery are summarized in Table 2.

[Comparison Examples 2 to 5]

The procedures of Example 1 were repeated except that only one of VC and PS was incorporated into the electrolytic solution.

The preparation and evaluation of the battery are summarized in Table 2.

Table 2
(Solvent: PC/DMC=1/2)

Example	Additive(s) (%)	Initial discharge capacity (relative value)	Discharge capacity retention
Example 1	VC(1.5)/PS(1.5)	0.97	94.8%
Com.Ex. 1	None	0	--
Com.Ex. 2	VC(1.5)	0.93	83.2%
Com.Ex. 3	VC(3.0)	0.95	84.8%
Com.Ex. 4	PS(1.5)	0.95	82.7%
Com.Ex. 5	PS(3.0)	0.96	84.3%

[Examples 2 & 3]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/DEC (1/2) (for Example 2), and that the solvent was replaced with EC/MEC (1/2) and the negative electrode was made from artificial graphite (for Example 3).

The preparation and evaluation of the battery are summarized in Table 3.

Table 3
(Additive: VC(1.5%)/PS(1.5%))

Example	Solvent (graphite)	Initial dis- charge capacity (relative value)	Discharge capacity retention
Example 2	EC/DEC=1/2 (natural)	1.02	95.3%
Example 3	EC/MEC=1/2 (artificial)	1.03	94.7%

[Examples 4 to 7]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (1/1/2) and that the amount of the added organic compounds were changed.

The preparation and evaluation of the battery are summarized in Table 4.

Table 4
(Solvent: EC/PC/DEC=1/1/2)

5	Example	Additives	Initial dis- charge capacity (relative value)	Discharge capacity retention
10	Example 4	VC(0.5)/PS(1.5)	1.01	93.5%
	Example 5	VC(3.0)/PS(1.5)	0.98	93.8%
	Example 6	VC(1.5)/PS(0.5)	1.00	93.1%
	Example 7	VC(1.5)/PS(3.0)	0.99	93.6%

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[Examples 8 and Comparison Examples 6 to 9]

20 The procedures of Example 1 were repeated except
that the solvent was replaced with EC/PC/DEC (3/1/6) and
that the natural graphite for the negative electrode was
replaced with artificial graphite.

The incorporation of the additives was examined
under various conditions.

25 The preparation and evaluation of the battery are
summarized in Table 5.

Table 5
(Solvent: EC/PC/DEC=3/1/6,
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 8	VC(1.5)/PS(1.5)	1.02	95.5%
Com.Ex. 6	None	1.00	81.6%
Com.Ex. 7	VC(1.5)	0.97	83.8%
Com.Ex. 8	PS(1.5)	1.00	84.2%
Com.Ex. 9	VC(10.0)/PS(10.0)	0.93	80.6%

[Example 9]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/MEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

Each of the additives of VC and PS were incorporated in an amount of 2.0 wt.%.

The preparation and evaluation of the battery are summarized in Table 6.

Table 6
(Solvent: EC/PC/MEC=3/1/6,
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 9	VC(2.0)/PS(2.0)	1.03	94.1%

[Example 10]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DMC/MIPC (3/1/3/3) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The preparation and evaluation of the battery are summarized in Table 7.

Table 7
(Solvent: EC/PC/DMC/MIPC (3/1/3/3),
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 10	VC(1.5)/PS(1.5)	1.01	93.4%

[Examples 11 & 12 and Comparison Example 10]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DMC/DEC (3/1/3/3), that LiCoO_2 (positive electrode active material) was replaced with LiMn_2O_4 , and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 8.

Table 8
(Solvent: EC/PC/DMC/DEC (3/1/3/3),
Positive electrode: LiMn_2O_4 ,
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 11	VC(1.5)/PS(1.5)	1.05	95.5%
Example 12	VC(1.5)/BS(1.5)	1.05	95.3%
Com.Ex. 10	BS(1.5)	1.00	83.4%

[Examples 13 to 19 and Comparison Examples 11 to 14]
The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 9.

Table 9
(Solvent: EC/PC/DEC (3/1/6),
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 13	VC(1.5)/PS(1.0)/BS(0.5)	1.03	95.8%
Example 14	VC(1.5)/BDDMS(1.5)	1.02	94.2%
Example 15	VC(1.5)/EGDMS(1.5)	1.01	93.7%
Example 16	VC(1.5)/BDDMS(1.0)/EGDMS(0.5)	1.02	94.9%
Example 17	PS(1.5)/BDDMS(1.5)	1.00	93.9%
Example 18	PS(1.5)/EGDMS(1.5)	1.00	93.3%
Example 19	PS(1.5)/BDDMS(1.0)/EGDMS(0.5)	1.01	94.5%
Com.Ex. 11	BDDMS(1.5)	1.01	82.9%
Com.Ex. 12	EGDMS(1.5)	1.01	82.3%
Com.Ex. 13	BDDMS(3.0)	1.01	83.9%
Com.Ex. 14	EGDMS(3.0)	1.01	83.1%

[Examples 20 to 25 and Comparison Examples 15 to 18]
The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 10.

Table 10
(Solvent: EC/PC/DEC (3/1/6),
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 20	VC(1.5)/MPGC(1.5)	1.00	92.3%
Example 21	VC(1.5)/PA(1.5)	1.00	91.5%
Example 22	VC(1.5)/MPGC(0.5) /PA(1.0)	1.01	92.9%
Example 23	PS(1.5)/MPGC(1.5)	1.01	92.0%
Example 24	PS(1.5)/PA(1.5)	1.01	90.9%
Example 25	PS(1.5)/MPGC(0.5) /PA(1.0)	1.02	92.5%
Com.Ex. 15	MPGC(1.5)	1.00	82.0%
Com.Ex. 16	PA(1.5)	1.00	81.9%
Com.Ex. 17	MPGC(3.0)	1.00	83.2%
Com.Ex. 18	PA(3.0)	1.00	82.9%

[Examples 26 to 28 and Comparison Examples 19 to 25]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 11.

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Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 26	VS (0.15) /BAOMC (2.0)	1.01	93.8%
Example 27	VS (0.2) /BAOMC (1.5)	1.00	94.0%
Example 28	VS (0.3) /BAOMC (1.5)	1.00	92.5%
Com.Ex. 19	VS (0.2)	1.00	83.5%
Com.Ex. 20	BAOMC (1.5)	1.00	83.2%
Com.Ex. 21	VS (1.7)	0.77	74.7%
Com.Ex. 22	BAOMC (1.7)	0.99	85.1%
Com.Ex. 23	VS (10.0) /BAOMC (10.0)	0.66	63.4%
Com.Ex. 24	BDDMS (1.5) /BAOMC (1.5)	1.00	83.2%
Com.Ex. 25	PA (1.5) /VS (0.2)	1.00	83.5%